PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Hydrocarbon Binders

We, STANDARD FRANCAISE DES PETROLES, a Body Corporate organised under the laws of France, of 82, Avenue des Champs Elysees, Paris, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known that the addition of a compound having one or more amino-groups improves the adhesivity of hydrocarbon binders in the presence of water. Fatty amines having more than 9 carbon atoms per molecule are commonly used. Such amines are expensive to make and need special equipment.

It is known that amido-amines obtained by condensing one molecule of an organic acid with one molecule of a polyamine by heating them together improve the adhesivity to materials of hydrocarbon binders in the presence of water.

Suitable acids for this process are saturated or unsaturated fatty acids having more than 8 carbon atoms per molecule, pure or mixed, such as palmitic, stearic, oleic, erucic or linoleic acids, fatty acids from palm oil, coconut oil, colza oil, cotton-seed oil, poppy seed oil, castor oil, fatty acids from wool grease, fish oils and other vegetable or animal fatty acids or mixtures of such acids. Tall oil (a residual acid obtained in paper manufacture), naphthenic acids, and natural or synthetic carboxylic acids generally may also be used.

In place of the fatty acids, the corresponding fatty oils may be used.

Suitable polyamines include ethylene diamine, diethylene diamine, triethylene diamine and in general amines having the formula $NH_2—R—NH_2$ where R is an aliphatic or aromatic radical. Complex compounds obtained by allowing ammonia to react with dichlorinated hydrocarbons (such as dichloroethane, dichloropropane and the like) are also suitable. In this class there occur such compounds as diethylene triamine and triethylene triamine.

The condensation reaction between the acid and the polyamine is carried out by heating at from 110° to 150° C. or higher. A temperature of 130—140° C. is generally suitable.

It has been shown that the active product produced by the condensation of one molecule of carboxylic acid with one of polyamine progressively loses its activity if the binder containing it is heated at temperatures in excess of 100° C. It may be imagined, for example, that the acid constituents of the binder react with the free amino group of the amido-amine to give an inactive amide product.

The Applicants have found that the adhesivity, in the presence of water, of bituminous compositions containing these amido-amine condensation products may be stabilised to heat by the addition of a minor amount of free polyamine.

The amount of amido-amine used may be from 0.1% to 10% of the bituminous compositions.

The amount of free polyamine may be from 1 to 200% of the amount of amido-amine.

A typical improved binder composition is as follows:

Cutback: (viscosity at 25° C. as measured by the Institute of Petroleum's Standard Test I.P.72=8/10) - - - - -	96.5%
Oleylamido-2 ethylene amine-1 -	2.5%
Ethylene diamine - - - - -	1%

This example is illustrative only and it is obvious that hydrocarbon binders of any

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Price 3s. 6d.

Price 4s 8d

type or viscosity may be used in accordance with the purpose in view. Equally, the nature and proportions of the active additives may be varied within the ranges already given.

The following purely illustrative examples will facilitate the understanding of the invention and the benefits derived from it.

EXAMPLE I.

A mixture of 1 mol of oleic acid and 1 mol of ethylene diamine are heated at 140° C., until foaming ceases (about 2 hours).

The product obtained in 3% solution in a liquid bitumen allows wet aggregate to be coated completely.

To test heat stability, the mixture is heated at 170° C. for several hours. Samples are withdrawn at intervals, and used for coating tests on wet aggregate. The coated aggregate is immersed in water, and the percentage surface still covered with binder at the end of 24 hours immersion is measured.

The results are given in Table I.

TABLE I.

Time of heating at 170° C. (hours)	% of Aggregate covered after 24 hours immersion
0	90%
3	95%
6	85%
9	40%
10	10%

EXAMPLE II.

The condensation product of Example I is dissolved in 3% concentration in a liquid binder. In addition 1% of ethylene diamine is added.

The blend is then heated at 170° C. as in Example I. The samples withdrawn gave the following results (Table II):

TABLE II.

Time of heating at 170° C. (hours)	% of Aggregate covered after 24 hours immersion
0	95%
3	98%
6	98%
9	98%
14	98%
20	75%

The Applicants have also found that there is a still greater increase in heat stability, and that the adhesivity is increased, when a soap of calcium or lead or other divalent metal is added to the mixture in an amount from 0.1 to 10% by weight based on the hydrocarbon binder.

The soap, a calcium soap for example, may be added to the binder itself, or to the acid-polyamine condensation product during or after its preparation. It may also be formed *in situ*.

The following illustrative example shows the improved results obtained with a calcium soap.

EXAMPLE III.

A liquid bitumen has added thereto 3% of a Tall-oil-ethylene diamine condensation product, 3% of calcium soap of Tall-oil and 1% of ethylene diamine. The mixture is treated at 170° C. as in the previous examples and samples withdrawn during heating. The results are given in Table III.

TABLE III.

Time of heating at 170° C. (hours)	% of Aggregate covered after 24 hours immersion
0	100%
3	100%
9	100%
14	100%
17	98%
20	98%

It can be useful to prepare a concentrate containing the various active stabilisers, this concentrate being easy to dissolve in a hydrocarbon binder.

The concentrate comprising carboxylic acid-polyamine condensation product and free polyamine, with or without calcium soaps, is a viscous liquid or a pasty solid. It tends to fume in air when it contains ethylene diamine as the free polyamine and is inconvenient and unpleasant to handle.

It has been found convenient to dilute the concentrate with a heavy oil fraction, either naphthenic or aromatic. This may be derived from petroleum, but preferably there is used a viscous synthetic oil obtained in the preparation of alkylated aromatic hydrocarbons by the Friedel Crafts synthesis.

Example IV gives a process for making up such a concentrate.

EXAMPLE IV.

A vessel provided with a mechanical stirrer is charged with 1300 kg. of Tall

oil and 519 kg. of ethylene diamine. The temperature is maintained for three hours at 130—140° C.

52 kg. of lime are then added, while keeping the temperature at 108—110° C., which forms the corresponding calcium soap.

Finally, there are added 1950 kg. of a viscous synthetic oil derived from the Fischer-Tropsel synthesis process.

The concentrate so obtained present in a concentration of 0.5 to 10% or more in a bituminous binder, gives excellent adhesivity in the presence of water, and a remarkable heat stability of its properties.

In summary, therefore, the present invention provides a bituminous composition having incorporated therein a minor proportion of a carboxylic acid-polyamine condensation product of amido-amine structure, together with a free polyamine. With monobasic acids and diamines the condensation product will have the general formula $R—CONH—R^1—NH_2$. The amount of free amine may be from 1 to 200% based on the condensation product (throughout the Specification and claims, all percentages are by weight unless otherwise specified), and the treating agent may be added to bitumen in amounts to give a condensation product concentration of 0.1 to 10% based on the bitumen. Naturally, when high concentrations of amido-amine are used the proportion of free polyamine will be relatively low.

What we claim is:—

1. A bituminous composition having incorporated therein a minor proportion of a carboxylic acid-polyamine condensation product of amido-amine structure together with a free polyamine.

2. A bituminous composition according to Claim 1, wherein the free polyamine is present in an amount from 1 to 200% based on the condensation product.

3. A bituminous composition according to Claim 1 or Claim 2, wherein there is also present a soap of a divalent metal.

4. A bituminous composition according to any of the preceding claims, wherein the active materials are dispersed in a heavy hydrocarbon oil of naphthenic or aromatic type.

5. A bituminous composition according to Claim 4, wherein the concentration of the condensation product is from 0.1 to 10% based on the bitumen.

6. A bituminous composition according to any of the preceding claims, wherein the condensation product is derived from animal or vegetable fatty acids having more than 8 carbon atoms per molecule, preferably oleic acid or Tall-oil.

7. A bituminous composition according to any of the preceding claims, wherein the polyamine component of the condensation product and/or the free polyamine is ethylene diamine.

8. A bituminous composition according to any of Claims 3 to 7, wherein the soap is a calcium soap.

9. A bituminous composition according to any of Claims 3 to 8, wherein the acid radical of the soap is the same as that of the condensation product and is preferably Tall-oil.

10. A bituminous composition as claimed in any of the preceding claims wherein the carboxylic acid-polyamine condensation product is prepared by heating equimolecular proportions of a higher fatty acid or mixtures thereof of the character described and a polyamine at a temperature above 110° C., and preferably below 150° C., until reaction ceases, and wherein the free polyamine is subsequently added to the amido-amine so formed.

11. A modification of the method of Claim 10, wherein the reaction is carried out in the presence of excess polyamine, whereby a blend of amido-amine and free polyamine is formed directly.

12. A method according to Claim 10, or Claim 11, wherein the reaction product is further heated with a basic compound of a divalent metal whereby a metal soap is formed.

13. A method according to any of Claims 10 to 12, wherein the acid is Tall-oil, the polyamide is ethylene diamine and the basic compound is lime.

14. The improved manufacture of bituminous compositions substantially as hereinbefore described.

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